Metal Complexes in Molecular Junctions.

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The use of metal complexes to achieve a conductive molecular junction with a special focus on organometallics is overviewed and illustrated with representative examples. The prospects offered by such compounds owing to their specific properties are discussed.

Introduction to metal–molecule–metal junctions

Single molecules as active elements have been considered as potential building blocks for future nanoelectronic systems because of their advantages in cost, scalability, component density, and power consumption.[1,2] However, it is unlikely that molecules will replace silicon based electronics, but rather complement this technology by providing novel functionalities leading to new features.[1] Therefore, the characteristics of the device should be controllable by choosing an appropriate design of molecules with the targeted properties, which allow infinite possibilities of development by chemical design. Note that the growth of molecular electronics is also dependent on the development of reliable methods for conductance measurements in metal–molecule–metal junctions, and on the improvement of junction characterization and of fabrication of simple operative devices.[2,3]

Designing and preparing molecular wires with a good charge transport performance is of primary interest to the development of molecular electronics. A molecular wire should consist of a molecular chain that allows strong electrode coupling between two electrodes attached to its chain ends in order to promote electron transfer through this bridge.[2,4] In this context, an exploration of charge transport with various techniques (mechanical break junctions (MBJ), scanning probe microscopies, nanogaps, *etc.*) has been carried out in order to understand the dependence of molecular conduction, *i.e.* of transport mechanism, on bonding architecture and molecular energy levels which will ultimately influence the design of molecular conductors.[2c,4] In a simple picture, a large difference between conduction orbitals of short molecules and the Fermi level of the metal electrode leads to simple nonresonant tunnelling of an electron through the molecule orbitals in a single step with no appreciable residence time of the electron on the molecule (Scheme 1). With a longer wire (usually larger than 3–5 nm), when the energy difference is smaller and the molecule–electrode coupling higher, Coulomb blockade behaviour through charging of the molecule can happen and charge transport occurs in two steps, *i.e.* metal to molecule and molecule to metal. Charges are thus injected into molecular orbitals and driven along the backbone by the applied field. This can lead to multistep

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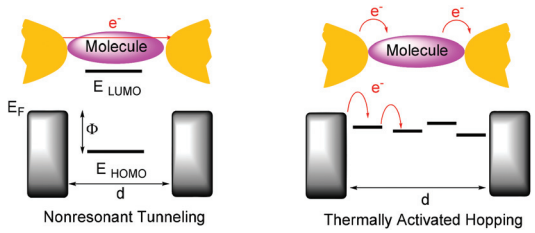
Stéphane Rigaut received his PhD in 1997 from the Université Bordeaux 1 under the supervision of Prof. Didier Astruc and Dr Marie-Hélène Delville on redox catalysis with electron-reservoir complexes. After a post-doctoral position in Minneapolis (USA) with Prof. Larry L. Miller to explore the vapoconductivity in dendrimers and swollen polymers, he was appointed in 1998 as an assistant professor at the Université de Rennes 1 where he mainly studied electron delocalization in organometallic carbon-rich complexes. Full Professor since 2008, he is now interested in the building and study of multifunctional organometallic molecular wires and switches for molecular electronics.



Scheme 1 Illustration of transport mechanisms.

hopping for large molecules through a series of discrete steps. This transport regime is thermally activated in contrast to tunnelling. Note that superexchange (tunnelling) and hopping are not mutually exclusive, both may be present.

In the tunneling regime, the molecular resistance varies exponentially with molecular length, $R = R_0 \exp(\beta d)$ where R_0 is the contact resistance, β is the tunneling decay constant, and d is the molecular length. Many studies have been carried out with organic π conjugated molecules, such as oligo(phenylene-ethynylene) (OPE), leading to attenuation factors of *ca.* 2–6 nm^{-1} (9 nm^{-1} for alkane thiols).[2c,4] When the molecular length exceeds a critical distance of *ca.* 4 nm, the tunneling efficiency is low and hopping conduction is dominant. Then, molecular resistance displays a relatively weak length dependence ($R \propto d$) leading to apparent β values of 0.2–0.6 nm^{-1}, and is dependent on the temperature and on the hopping barrier ($R \propto \exp(E_a/kT)$).[4]

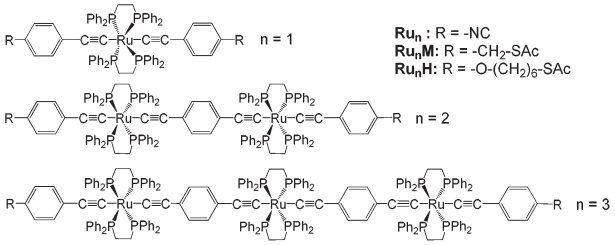
Molecular junctions with metal complexes

Wires incorporating metal complexes are particularly interesting because they can offer various structures with high ground spin states and low HOMO–LUMO gap. Furthermore, redox active complexes can lead to multiple redox and spin states that can afford unusual current–voltage characteristics, observation of the electron/electron or hole/hole correlation effect, as well as efficient charge conduction. Furthermore, the redox processes might enable gated control of electronic functions and, associated with the optical, redox and magnetic characteristics of the complex and/or of specific associated ligands, the development of multifunctional devices addressable with electrons or photons that would lead to a modification of the *I–V* response to achieve attractive molecular junctions for spintronic and optoelectronic applications.[5]

Incorporating several metal centres into a rigid molecular backbone can easily lead to very long molecular wires (typically over 4 nm). For example, *in situ* self-assembled monolayers on the surface of bisterpyridine based transition metal complexes *via* sequential stepwise coordination of metal ions allowed the easy achievement of multilayered systems toward 3D nanoarchitectures displaying very low attenuation factors.[6] Rampi *et al.* reported electrical measurements of such metal incorporated nanowires up to 40 nm in length with extremely low β values of 0.28 nm^{-1} (Fe^{II}) and 0.01 nm^{-1} (Co^{II}) implicating a multistep charge hopping process between the metal centres in the backbone.[7] Thus conductivity does not decrease significantly with length and depends on the metal atom. Wires up to 5 nm incorporating Zn porphyrins were also found to display very low attenuation factors (0.4 nm^{-1}).[8]

The organometallic approach

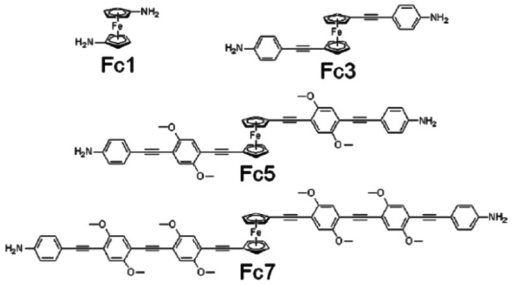
Organometallic complexes represent attractive materials that have received less attention, despite the fact that large



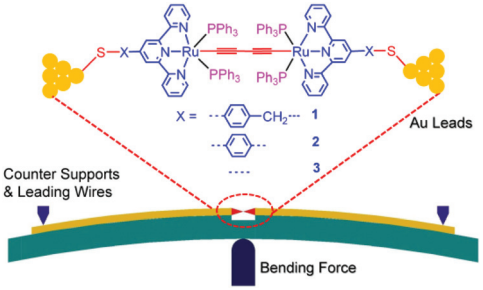
Scheme 2 Ruthenium acetylide wires.

functional molecules can be easily built to be directly included in junctions. Depending on the metals and the ligands, the character of the redox orbitals can be varied from metal to ligand. Therefore, the electronic coupling between these different elements of the molecule as well as the charge state will adjust its HOMO–LUMO level with the Fermi level of the electrodes.[9] Importantly, complexes with extensive mixing of the metal based orbitals with both the supporting and bridging ligands, *i.e.* with a better degree of electronic delocalization along the molecular backbones such as ruthenium ones,[9a–c] are expected to exhibit a weaker dependence of the charge transport on molecular length, giving an opportunity to develop alternative materials.

Our group reported the electrical transport behavior of a series of ruthenium redox-active conjugated molecular wires as a function of temperature and molecular length (Scheme 2), using conducting probe atomic force microscopy and crossed-wire junctions.[10] The wires consist of covalently coupled ruthenium(II) bis(σ-arylacetylide) complexes (**Ru1**–**Ru3**) with strong electronic coupling between the carbon-rich ligands, and length ranging from 2.4 to 4.9 nm. We found a very weak dependence of the wire resistance on molecular length, consistent with a high degree of electronic communication along the molecular backbone (β = 0.9 nm^{-1}). In low-temperature (5 K) experiments, Coulomb blockade like behavior was observed in junctions incorporating **Ru3** suggesting a hopping mechanism while direct tunneling appears to be the dominant transport mechanism in **Ru1** and **Ru2** junctions. This was consistent with a study of Wang *et al.* that compared *trans*-Ru-$(PPh_2CH_2PPh_2)_2(C{\equiv}CC_6H_4{-}SAc)_2$ with the well-studied oligo-(1,4-phenylene ethynylene) (OPE), and that reported a lower electronic decay constant as well as a higher conductance for the complex ascribed to a lower band gap between its HOMO and the gold Fermi level.[11] Our further studies with the related complexes **Ru$_n$H** and **Ru$_n$M** (Scheme 2) revealed that the charge transport in **Ru$_n$M** junctions was direct tunneling, but in **Ru$_n$M** (n = 2, 3) junctions, the mechanism was thermally activated hopping, as shown with the temperature-dependent conduction measurements.[12] As expected the long insulating chains favor the hopping process. Importantly, the derived activation energy values, of 0.17 eV for **Ru$_2$H** and 0.14 eV for **Ru$_3$H**, are significantly lower than those previously reported for organic compounds (0.3 to 0.6 eV) which can be expected from the low oxidation potential of the wires and perhaps greater electron delocalization. Note



Scheme 3 Ferrocene in OPEs. Reprinted with permission from ref. 15. Copyright 2013 ACS.



Scheme 4 Au–molecule–Au junctions constructed with a three-point bending mechanism.[17]

that the study of electronic transport through the related redox-active diruthenium(III) tetra(2-anilinopyridinate)-di-(4-thiolphenylethynyl) (*trans*-$Ru_2(ap)_4((C{\equiv}CC_6H_4)_2S{-})_2$ complex in a nanogap also suggested that charge storage occurs in the molecule with the observation of hysteresis in the *I–V* curves.[13]

Though the potential of such structures has already been suggested,[14] a recent STM/CP-AFM study clearly showed that incorporation of ferrocene in the OPE backbone terminated with amino groups (Scheme 3) also leads to an enhancement of molecular conductance of OPE wires in the tunnelling and hopping regimes,[15] and that the enhancement of the hopping regime is higher than that of the tunnelling regime. The authors even found that the conductance of a long molecule in the hopping regime (**Fc5**) is higher than that of the shorter **Fc3** in the tunnelling regime at room temperature, and that the hopping activation energies are lower for these ferrocene adducts (*ca.* 0.3 eV) in comparison to their purely organic OPE counterparts (0.6 eV). Therefore, they give rise to higher total molecular conductance probably involving several discrete hopping steps, thanks to ferrocenium/ferrocene interactions allowing rapid intramolecular electron transfer. CP-AFM measurements on another series of ethynyl ferrocenyl molecules $AcS{-}C_6H_4{-}C{\equiv}C{-}(Fc)_n{-}C{\equiv}C{-}C_6H_4{-}SAc$ (n = 2, 3) self-assembled on Au(111) surfaces with two or three conjugated ferrocenyl units revealed clear Coulomb blockade behaviour arising from the capacitive charging of molecules at room temperature.[16] The current increases in steps with the bias voltage suggesting charge injections in the molecules (Fe^{II} to Fe^{III}), and the resistances of the mono oxidized species are lower than those of aliphatic, polyolefinic and aromatic molecules of similar length. The authors also ascribe this to the formed mixed valence species in which rapid intramolecular electron hopping occurs.

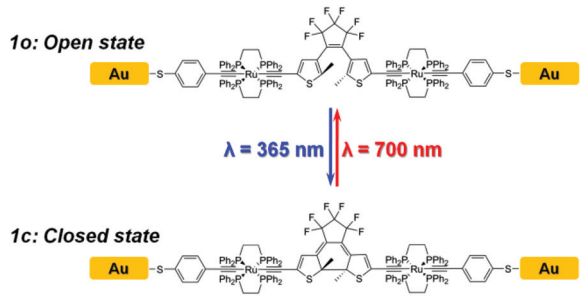
More recently, using electrochemically assisted MBJ (Scheme 4), a single-molecule study of diruthenium(II) coordinated molecules containing two Ru(II) redox centers linked by 1,3-butadiyne showed significantly higher conductance for these molecules than for OPEs of similar lengths under the same experimental conditions (one order of magnitude for **3**), as well as a weaker length dependence.[17] Based on the HOMO-mediated hole tunnelling mechanism, the authors assign this to the better energy match of the Fermi level of gold electrodes with the HOMO mainly located on the $Ru{-}C{\equiv}C{-}C{\equiv}C{-}Ru$ backbone. They also found that conductance should more likely be influenced by modification of the 1,3-butadiyne bridge because electronic communication between the two redox centers is modified, rather than by modification of the ancillary terpyridyl ligand that shows only a minor contribution to the HOMO.

Other intriguing measurements of molecular junctions have recently been reported for functional molecules that consist of Fc-alkanethiol ($SC_{11}Fc$) using gallium oxide interlayer-based junctions. The molecular junctions were able to rectify the current with large rectification ratios (*ca.* 90–180 for 1 V), whereas a junction lacking the Fc moiety ($SC_{n-1}CH_3$) did not rectify significantly the current. The mechanism of rectification with Fc-terminated SAMs seems to be charge transport processes that change with the polarity of the bias: from tunneling (at one bias) to hopping combined with tunnelling (at the opposite bias).[18]

Functional molecular junctions with metal complexes

The active control of the molecule properties inside molecular junctions allows the tuning of molecular conductance, and hence the potential achievement of functional molecular junctions and logic gates.[3,19,20] As mentioned above, upon oxidation or reduction of the active molecule, the current can be directly modulated by an external voltage (gate) with direct molecular orbital gating. Recently, such a true molecular transistor was described with 1,4-benzenedithiol that enhances the prospects for such molecular electronic devices.[19] The potential of coordination metal complexes in that domain was demonstrated in 2002 with a Co ion in $[Co(tpy\text{-}(CH_2)_5{-}SH)_2]^{2+}$ that can act as a single-electron transistor,[20] and more recently, for example, with multi-level conductance switching of a monolayer of redox active thiol linked Fe^{II}, Ru^{II}, and Co^{II} biphenylterpyridine complexes showing multiple electroreduction for multi-bit storage.[21]

Electrochemically gated molecular junctions have also been realized to achieve conductivity modulation of organic and metal complexes.[22,23] For example, with a ferrocene unit terminated with two cysteamine groups, Tao *et al.* showed that with



Scheme 5 Isomerization under light irradiation of a ruthenium acetylide/DTE compound bonded into a nanogap.[26]

an electrochemical gate set at 0.6 V the current increases by one order of magnitude. This gate effect is ascribed to oxidation of the molecule when its HOMO is raised to the Fermi level of the electrode.[22] Another tunnelling junction of 6-thiohexanoylferrocene immobilized on an Au(111) in an electrochemical (STM) set up was also achieved.[24] This junction exhibits an enhanced tunnelling current upon alignment of the tip and substrate Fermi levels with the molecular redox state. The transistor and diode like current voltage responses also observed were attributed to the redox process of the ferrocene moiety.

A promising means to achieve memories or logic gates in a molecular junction is by the use of photochrome-coupled metal complexes to produce an original single molecule behaviour that would gather the properties of both units and/or synergetic properties.[25] In that direction, we recently developed a photo-modulatable molecular transport junction *via* on-wire lithography-fabricated nanogaps functionalized with a dithienylethene (DTE) unit bearing two ruthenium fragments (Scheme 5).[26] Although the switching rates need to be improved for practical applications, a reversible and repeatable bi-state conductive switching upon alternate irradiation of UV and visible light could be distinctly observed. Theoretical calculations further suggest: (i) that the ruthenium acetylide moieties adjust judiciously the electronic coupling of the DTE fragment with the metal electrodes, avoiding electrode quenching of excited states upon irradiation as usually observed with metallic electrodes, and (ii) that the delocalization of the HOMO of the closed isomer lying near the Fermi level of the junction is high enough to lead to an efficient conductivity. The switching in conductivity is explained by a weak delocalization in the photochromic part added to the polarization of the HOMO level of the open form.[21] In addition to this photochromic property, we previously showed that such a ruthenium/DTE association can also perform electrochemical cyclization of the DTE unit in solution, at low potential, in contrast to organic systems.[27] Therefore, the association of these two stimuli in a single device should allow the achievement of multifunctional molecular transport junctions (MTJs) addressable with light and electron transfer.

Another interesting field concerns the association of magnetic properties of complexes with molecular junctions. The electrical manipulation of the spin state with a Mn bis-terpyridine complex, *i.e.* a high-spin (S = 5/2) to low-spin (S = 1/2) transition, was recently realized in a three-terminal device.[28] By adjusting the gate-voltage, the terpyridine moiety is reduced and thereby strengthens the ligand-field on the Mn-atom to stabilize the low-spin configuration. Then, the corresponding sequential tunnelling current is suppressed by a change in spin configuration (spin blockade). More recently, spin state dependence of the conductivity of the spin crossover compounds $[Fe(Htrz)_2(trz)](BF_4)$ (Htrz = 1H-1,2,4-triazole)[29a] and $[Fe(trz)_3](BF_4)_2$ [29b] was established with temperature and also with voltage for the latter. For $[Fe(Htrz)_2(trz)](BF_4)$, the low spin state is characterized by higher conductance and lower thermal activation energy of the conductivity. These results, combined with another recent report on the redox conductivity switching between a high and a low conductive state of the spin coated film of a Rh^{III} complex associated with an organic radical, shows the promising potential of (organometallic) transition metal complexes in molecular junctions.[30]

Outlook

On the basis of all these studies, metal complexes obviously have a great deal of potential applications in future molecular-based electronic technology. Indeed, the studies presented are a clear validation of a strategy that consists in the attainment of molecular wires *via* metal incorporation into the backbone of organic wires to improve the conductivity features. Furthermore, they contribute to a precise rationalisation of the transport mechanisms, for example, by identification of the factors that favour hopping over tunnelling.

It has also been demonstrated that the redox properties of the complexes permit the control of conductivity of devices, though much progress and many discoveries remain to be achieved. As an example, metal complexes can display very low HOMO–LUMO gap and are excellent candidates for achieving ambipolar single molecule field-effect transistors than can be switched between n-type and p-type transport behaviour with a gate voltage.[31]

Light controlled metal complexes or the association of complexes with light controlled active units is also promising for conductivity gating. Recently, light-induced modulation of molecular conductance was realized with a porphyrin-C_{60} dyad.[32] Conductivity increases owing to charge separation under illumination and returns to lower conductivity in the dark. The potential of metal complexes in that field is vast, especially with metals such as Pt that promote more highly conjugated excited states.

Metal complexes have also been involved in molecular recognition and sensing, and thus also constitute promising systems from the perspective of building a molecular circuit combining fluidic channels to analyse substances *via* conductivity modulation.[33]

In conclusion, as a high level of functionality may be integrated into a molecular system permitting redox or

photochemical addressing, and given the reversible redox processes associated with the vast collection of metal–ligand combinations, there is plenty of room for improvement and development of original functional molecular junctions integrating organometallics as well as coordination compounds.

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